The Temperature Dependence of the Limiting Conductances of the Aqueous Solutions of Some Aromatic Sulfonates

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In a previous paper⁽¹⁾, it was reported that hydrophobic bonding plays an important role in the association of the dye ion. It is thought that the transport properties of such organic ions as the dye ion will be influenced by the ice-like structure of water around the non-polar group. These transport properties will also be affected by the interaction between water and the ionized group of organic ions. In this investigation, the limiting equivalent conductances will be obtained for sodium salts of benzenesulfonic (to be abbreviated BSNa), α-naphthalenesulfonic (NSNa), *m*-benzenedisulfonic (BDSNa), and 1,5-naphthalenedisulfonic (NDSNa) acids at 35, 45, and 55°C (and at 25°C for NSNa), and the activation energies of the limiting mobilities for these sulfonate ions, *U*, will be calculated.

Experimental

Sodium sulfonates were decolorised with active carbon and recrystallized four times for BSNa, NSNa, and NDSNa (G. R. Tokyo Kasei Co.) or six times BDSNa (technical grade) from a water-ethanol solution and dried at 110°C over phosphorus pentoxide.

The experimental method of conductance has been reported elsewhere.⁽¹⁾

Results and Discussion

The limiting equivalent conductances, λ°, of sulfonates were obtained by the Fuoss-Onsager extended equation:

$$\lambda=\lambda^\circ-SC^{1/2}+EC\log C+JC$$

The symbols are as defined by Fuoss and Accascina.⁽²⁾ The limiting mobilities, λ_-°, of sulfonate ions were obtained from these limiting conductances.⁽³⁾ The activation energies, *U*, of sulfonate ions were calculated from the temperature dependence of their limiting mobilities. The plots of $\log\lambda^\circ$ against $1/T$ are linear for all sulfonate ions in the range of experimental temperatures; thus the activation energies are independent of the temperature. The results are given in Table I. In Table I the radii, *r*, of the equivalent spheres obtained from models based on Pauling⁽⁴⁾ are given also.

As may be seen from Table I, the relation between the activation energy of the limiting mobility and the ionic radius is not linear. Though the ionic radius of BDS^{-2} is nearly

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1) H. Uedaira and H. Uedaira, *Kolloid-Z. Z. für Polym.*, **194**, 148 (1964).

2) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Academic Press, N. Y. (1960).

3) The values of $\lambda_+^\circ(Na^+)$ were taken from R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworth, London (1959), p. 465.

4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y. (1960), Chapters 5 and 10.

TABLE I. THE LIMITING MOBILITIES AT VARIOUS TEMPERATURES AND ACTIVATION ENERGIES OF SULFONATE IONS

Ion	Temp. °C	λ°_- $cm^2\Omega^{-1}$ $equiv^{-1}$	r Å	U kcal.· mol^{-1}
BS^-	25	34.9[5a)]	3.50	3.36
	35	41.8		
	45	50.0		
	55	58.7		
NS^-	25	29.3	3.71	3.75
	35	36.6		
	45	43.6		
	55	52.4		
BDS^{2-}	25	59.9[5b)]	3.70	3.32
	35	70.0		
	45	85.9		
	55	99.8		
NDS^{2-}	35	57.8	3.89	3.54
	45	70.0		
	55	82.6		

equal to that of NS^-, the value of U for the former is smaller than that for the latter. Consequently, the activation energy depends not only on the size of the ion, but also on the ion-solvent interaction.

An aromatic sulfonate ion differs from an inorganic ion in having both a hydrophobic part (aromatic ring) and a hydrophilic part (sulfonic group). Each of the two parts has a different interaction with water. The aromatic part increases the ice-like structure of the watar in its neighborhood.[6,7)] Therefore, the local viscosity of the water in this region should be higher than that of bulk water. According to Samoilov,[8)] the activation energy of the ion transport depends upon the exchange of water molecules in the immediate neighborhood of the ion. As the frequency of the exchange of water molecules around the aromatic ring should be smaller than that of bulk water, the sulfonate ion with the larger aromatic ring has the larger activation energy, and the smaller mobility.

The sulfonic group is considered to be a mono-valent ion with a large radius, and the nearest neighbor water molecules around such ions become more mobile than in pure water because of the destruction of the structure of water by the ionic field.[8)]

It is interesting to compare the limiting mobility of the BS^- ion with that of the benzoate ion. The limiting mobility at 25°C and the activation energy of the benzoate ion are 32.5 $cm^2\Omega^{-1}equiv^{-1}$ and 4.21 kcal. mol^{-1} respectively,[9)] and its ion radius is 3.35 Å. Though the benzoate ion is smaller than the BS^- ion, the former has the smaller mobility and the larger activation energy. Gurney[10)] suggested that the water structure close to the carboxyl group is in order. Consequently, the frequency of the exchange of the water around the carboxyl group is smaller than that of bulk water. The difference between the limiting mobilities of the BS^- ion and the benzoate ion is explained by the structure-breaking effect of the sulfonic group. The sulfonic group will also partially break out the ice-like structure around the aromatic ring.

Thus, it is clear that the activation energy of the NS^- ion is the largest and that of the BDS^{2-} ion is the smallest, and that the mobility of the NS^- ion is the smallest and that of the BDS^{2-} ion is the largest. The interactions between the water and hydrophobic part and the ionized group of organic ions play important roles in the transport properties.

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5) a) M. Yokoi and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 4367 (1961); b) G. Atkinson, M. Yokoi and C. J. Hallada, ibid., **83**, 1570 (1961).

6) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

7) G. Neméthy and H. A. Scherage, ibid., **36**, 3401 (1962).

8) O. Ya. Samoilov, *Discussions Faraday Soc.*, **24**, 141 (1957). "Struktura Vodn'kh Rastvorov Elektrolitov i Gidrataziya Ionov," Moskva (1957), Glava 3.

9) Landolt-Börnstein Tabellen, 6 Auflage, 2 Band, 7 Teil II, Spriger Verlag, Berlin, 1960, p. 267.

10) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, N.Y. (1953), Chap. 9.